Thermodynamics: the basics

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Laws of Thermodynamics

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0 The Zeroth Law
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The Minus First Law

- AKA *The Equilibrium Principle* (Brown and Uffink 2001)
    - *An isolated system in an arbitrary initial state within a finite fixed volume will spontaneously attain a unique state of equilibrium.*
- Examples:
    - Thermal Equilibration
    - Equilibration of pressure
    - Chemical reactions
- *Worth emphasizing*: the adverb “quickly” does not appear in the above statement of the Law, and relaxation times vary widely.
- According to Brown and Uffink, it is this law that is the source of temporal asymmetry in thermodynamics.

The Zeroth Law

- We can place objects into thermal contact with each other.
- If A and B are brought into thermal contact, then one of three things will happen as the new system equilibrates:
  1. Heat flows from A to B.
  2. Heat flows from B to A.
  3. No heat flow.
- The Zeroth Law says that condition (3) is transitive:

  > *If A can be brought into thermal contact with B without heat flow, and B can be brought into thermal contact with C without heat flow, then A can be brought into thermal contact with C without heat flow.*

Zeroth Law and Equitemperature

If A can be brought into thermal contact with B without heat flow, and B can be brought into thermal contact with C without heat flow, then A can be brought into thermal contact with C without heat flow.

- This allows us to define an equivalence relation on equilibrium states: If A and B are equilibrium states, these states are equitemperature states iff A and B can be brought into thermal contact with each other with no heat flow.
- Note: we don't yet have a numerical temperature scale.

The First Law

- The work I do on a system in changing its state from a to b is

$$W = -\int_a^b \mathbf{F} \cdot d\mathbf{x},$$

  where **F** is the force opposing my efforts.
    - W positive = I do work on the system.
    - W negative = the system does work on me.
- I can also transfer energy to the system as heat.
- The First Law says that, if work W is done on a system, and heat Q passes into it, then the internal energy U of the system changes by an amount

$$\Delta U = Q + W.$$

- Differential form:

$$dU = đQ + đW$$

In a washroom in a physics building

The Second Law

- Kelvin (1851):

  > *It is impossible, by means of inanimate material agency, to derive mechanical effect from any portion of matter by cooling it below the temperature of the coldest of the surrounding objects.*

- Clausius (1854):

  > *Heat can never pass from a colder body to a warmer body without some other change, connected therewith, occurring at the same time.*

  > *Es kann nie Wärme aus einem kälteren Körper übergehen, wenn nicht gleichzeitig eine andere damit zusammenhängende Aenderung eintritt.*

QSR processes

- We distinguish between
    - Quasistatic, reversible processes
    - All other processes (dissipative processes)

Carnot's theorem

- Suppose we have a heat engine that
  1. Extracts an amount of heat Q_{in} from a hot reservoir;
  2. Performs net work W on its surroundings;
  3. Discards heat Q_{out} into a cold reservoir
- Define *efficiency*:

$$\eta = \frac{W}{Q_{in}} = 1 - \frac{Q_{out}}{Q_{in}}$$

- If we assume the 2nd Law as an axiom, it follows that

> *Any two heat engines operating in a qsr manner between two heat reservoirs have the same efficiency, which is dependent only on the temperature of the two reservoirs. Moreover, any other heat engine has lower efficiency.*

Absolute Temperature

- If η_{AB} is the efficiency of a reversible engine operating between reservoirs A, B, define the *thermodynamic temperature* T by

$$\frac{T_B}{T_A} =_{df} 1 - \eta_{AB}.$$

- This defines a temperature scale up to an arbitrary scale factor.

Ideal Gases

- An *ideal gas* satisfies:
    - *Joule's law.* The internal energy of the gas is a function only of temperature.
    - *Boyle's law.* At fixed temperature,

$$p \propto \frac{1}{V}.$$

Ideal gas thermometry

- Define ideal gas temperature θ by

$$\theta \propto pV.$$

- This gives us the equation of state, the *ideal gas law*:

$$pV = nR\theta,$$

where n is the ratio of the amount of gas in our sample to a standard reference quantity (1 mole), and R depends only on choice of units (ideal gas constant).

Comparing the two temperature scales

- What is the relation between the thermodynamic temperature T and the ideal gas temperature θ?
- Strategy:
    - Consider an ideal gas heat engine running between two heat reservoirs with i.g. temps θ_H and θ_C.
    - Pick a reversible cycle that's particularly easy to analyze.
    - Considering this cycle, we can get the efficiency $\eta(\theta_H, \theta_C)$ as a function of the ideal gas temperatures of our reservoirs.
    - Setting

$$\eta(\theta_H, \theta_C) = 1 - \frac{T_C}{T_H}$$

gives us a relation between the two scales.

Carnot cycle: the punchline

- Analysis of the Carnot cycle yields

$$\frac{Q_{in}}{\theta_H} = \frac{Q_{out}}{\theta_C}.$$

- or,

$$\eta(\theta_H, \theta_C) = 1 - \frac{Q_{out}}{Q_{in}} = 1 - \frac{\theta_C}{\theta_H}.$$

- Compare

$$\eta = 1 - \frac{T_C}{T_H}$$

.

- This gives

$$\theta \propto T.$$

Enter entropy

- For a Carnot cycle,

$$\oint \frac{đQ}{T} = \frac{Q_{in}}{\theta_H} - \frac{Q_{out}}{\theta_C} = 0.$$

- Moreover, this must be true for any qsr cycle.
- It follows that there is a state function S such that for any qsr process

$$\int_a^b \frac{đQ}{T} = S_b - S_a,$$

- or,

$$dS = \left(\frac{đQ}{T}\right)_{qsr}.$$

- This state function is called the *thermodynamic entropy*.

Entropy and the Second Law

- This gives us another way of stating the Second Law of Thermodynamics. For any cycle,

  $$\oint \frac{đQ}{T} \leq 0,$$

  with equality holding for reversible processes.
- In differential form,

  $$đQ \leq TdS,$$

  with equality holding for reversible processes.
- For any processes occurring within an adiabatically isolated system,

  $$dS \geq 0.$$

Entropy of an Ideal Gas

- Entropy difference between states *a* and *b* of an ideal gas is

$$S_b - S_a = nR \log\left(\frac{V_b}{V_a}\right) + C_V \log\left(\frac{T_b}{T_a}\right).$$

The Third Law

- No finite sequence of cyclic processes can succeed in cooling a body down to absolute zero.
- The entropy of every pure, crystalline substance approaches the same value as the temperature approaches zero.
- This gives us a natural zero-point for entropy.